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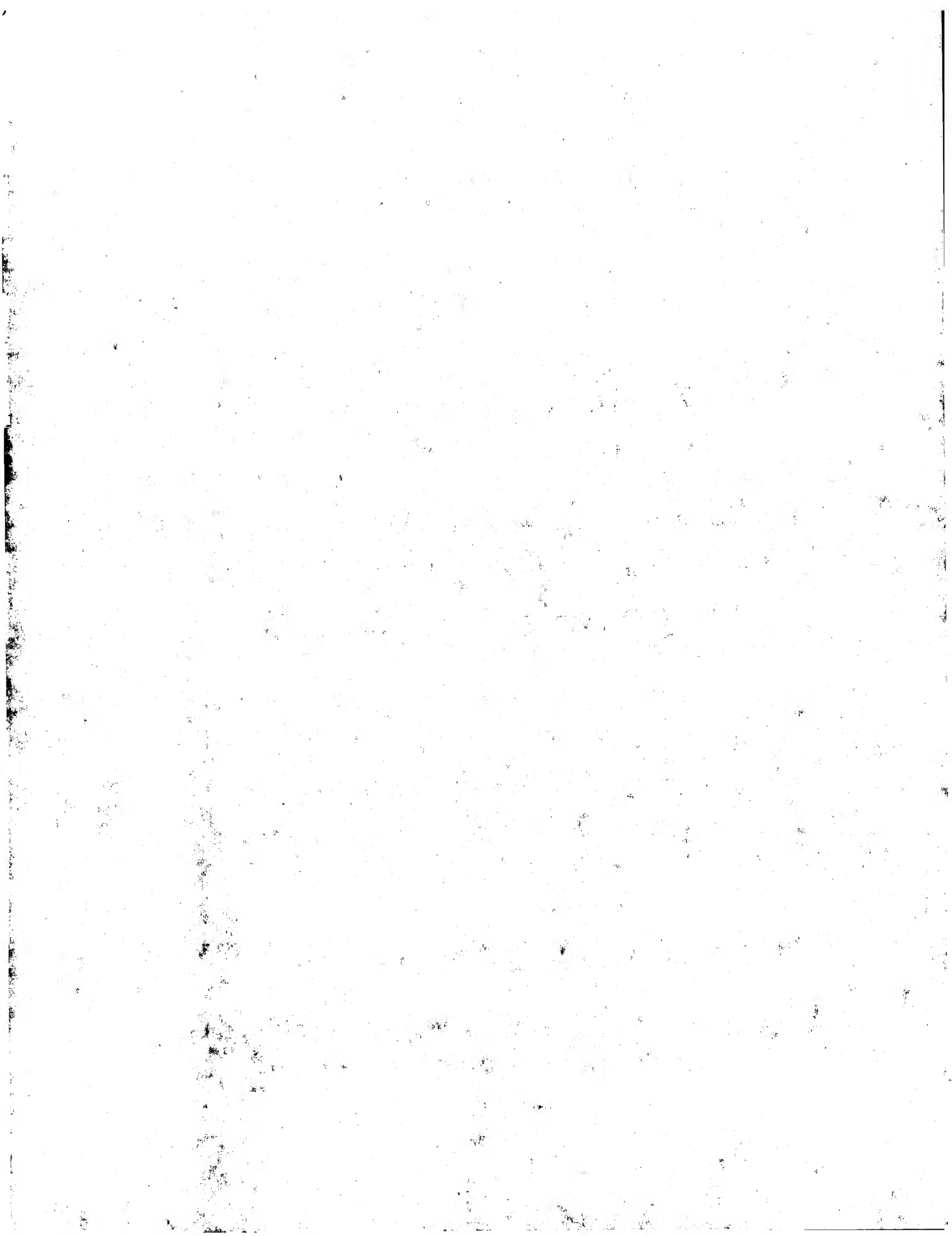
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Publication number: **0 429 307 A2**

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## EUROPEAN PATENT APPLICATION

⑪ Application number: 90312699.3

⑤ Int. Cl. 5: **C08F 283/06, C08L 51/08,  
C11D 3/37, C02F 1/56**

⑫ Date of filing: 21.11.90

③ Priority: 22.11.89 US 441122

④ Date of publication of application:  
29.05.91 Bulletin 91/22

⑧ Designated Contracting States:  
**AT BE CH DE DK ES FR GB GR IT LI LU NL SE**

⑦ Applicant: **ROHM AND HAAS COMPANY**  
Independence Mall West  
Philadelphia Pennsylvania 19105(US)

⑦ Inventor: Hughes, Kathleen Anne  
835 Cathcart Road  
Blue Bell, Pennsylvania 19422(US)  
Inventor: Swift, Graham  
901 Cross Lane  
Blue Bell, Pennsylvania 19422(US)

⑦ Representative: Tanner, James Percival et al  
**ROHM AND HAAS (UK) LTD.** European  
Operations Patent Department Lennig House  
2 Mason's Avenue  
Croydon, Surrey, CR9 3NB(GB)

⑤ Biodegradable, water-soluble graft copolymers, compositions containing such copolymers, and methods of use of such copolymers.

⑦ This invention is concerned with biodegradable water-soluble graft copolymers having building, anti-filming, dispersing and threshold crystal inhibiting properties, the copolymers comprising, grafted to a biodegradable substrate comprising polyalkylene oxide and/or polyalkoxylated materials, (a) acid-functional monomer(s), and, optionally, (b) other ethylenically unsaturated monomer(s) copolymerizable with (a).

The invention is also concerned with a process for preparing the graft copolymers, compositions comprising the graft copolymers, and with the use of such copolymers/compositions.

**EP 0 429 307 A2**

# **BIODEGRADABLE, WATER-SOLUBLE GRAFT COPOLYMERS, COMPOSITIONS CONTAINING SUCH COPOLYMERS, AND METHODS OF USE OF SUCH COPOLYMERS**

The present invention is concerned with graft copolymers and, more particularly, to graft copolymers prepared by grafting acid-functional monomers onto biodegradable polyalkylene oxides and polyalkoxylated substrates. These graft copolymers are biodegradable and are useful preferably as detergent additive polymers acting as builders, anti-filming agents, dispersants, sequestering agents and incrustation inhibitors. The term detergent, as used herein, includes textile laundering detergents, hard surface cleaners, such as formulations used in automatic dishwashers, and other compositions useful as cleaners.

In detergent applications, large volumes of chemicals are used. Because these chemicals may eventually enter the environment and reside in subsurface waters or open bodies of surface waters, it is highly desirable for such chemicals to be degradable in order to eliminate any environmental problems. Traditionally, detergents and cleaning agents have contained phosphates. These phosphates are added as detergent builders, acting to sequester alkaline earth metal hardness ions, as incrustation inhibitors and as antiredeposition agents. Despite the fact that the well known inorganic phosphorus compounds are highly effective and relatively non-toxic, they lead to environmental problems such as causing excess plant growth, resulting in eutrophication of lakes.

During the past three decades, efforts have been made in the detergent industry to convert from the eutrophying polyphosphates to more environmentally acceptable materials such as polycarboxylic acid polymers (e.g., polyacrylic acids). In a similar situation, the ubiquitous branched alkyl benzene sulfonates (ABS), probably the most popular surfactants, were replaced by their biodegradable linear counterparts (LAS) to eliminate build-up in surface and subsurface waters.

While the polycarboxylic acid polymers and copolymers currently used in detergents and water treatment applications do not suffer from the same drawbacks as the phosphorus-containing inorganic builders or the foam producing ABS surfactants, the past has taught that it is most desirable that chemicals, used in large volume applications which enter the environment, be biodegradable. Unfortunately, most polycarboxylic acid polymers and copolymers useful in detergent applications or as dispersants or as water treatment chemicals are not highly biodegradable.

Some effort has been made to provide biodegradable water-soluble polymers through the use of comonomers containing two ethylenically unsaturated double bonds. Notable in this regard is EP-A-0 291 808 (BASF Aktiengesellschaft). Disclosed in EP-A-0 291 808 are water-soluble copolymers prepared by the copolymerization of monomer mixtures of at least one monoethylenically unsaturated monocarboxylic acid, at least one comonomer containing at least two ethylenically unsaturated non-conjugated double bonds and at least one COO-X group, and, optionally, at least one monoethylenically unsaturated dicarboxylic acid, and/or at least one hydroxyl ester of a monoethylenically unsaturated carboxylic acid, and/or other water-soluble monoethylenically unsaturated monomers. However, studies of these polymers have revealed that they are difficult to make and do not combine the balance of good performance properties and biodegradability.

US-A- 4,746,456 ('456) discloses a detergent composition containing a graft copolymer of polyalkylene oxides and vinyl acetate which purportedly acts as a soil redeposition inhibitor. The detergent composition disclosed in the '456 patent contains from 0.1 to 3% of the graft copolymer obtained from grafting, onto a polyalkylene oxide polymer of ethylene oxide, propylene oxide or butylene oxide, vinyl acetate in a weight ratio of from 1:0.2 to 1:10. However, the detergent compositions of the '456 patent still contain phosphate along with this soil redeposition inhibitor and these graft copolymers are not readily biodegradable.

We have now unexpectedly found that graft copolymers, prepared by grafting acid-functional monomers onto biodegradable polyalkylene oxide and polyalkoxylated substrates, form graft copolymers which are biodegradable and are useful as detergent additives. These graft copolymers are particularly biodegradable when they are prepared by a process which yields short chain graft units. Such short chain graft units may be obtained by utilizing a metal salt, preferably a salt generating copper ions.

It is an object of the present invention to provide novel water-soluble polymers of acid-functional monomers grafted onto polyalkylene oxides. It is a further object of this invention to provide novel biodegradable graft copolymers. It is a still further object of this invention to provide a detergent formulation and a method of inhibiting scale formation utilizing said novel biodegradable graft copolymers.

According to the present invention there is provided a biodegradable water-soluble graft copolymer having building, dispersing and threshold inhibiting properties, which comprises (a) one or more acid-functional monomer, and, optionally, (b) one or more other ethylenically, e.g. monoethylenically, unsaturated monomer copolymerizable with (a), said monomer or monomers being grafted to a biodegradable substrate,

said substrate being selected from polyalkylene oxides, polyalkoxylated materials and mixtures thereof, and said copolymer being at least 25 percent biodegradable (ie having a biological oxygen demand (BOD) of at least 25 percent).

The present invention also provides a composition comprising a graft copolymer according to the invention, and an inert carrier or diluent.

The graft copolymers of the present invention are biodegradable and are useful as detergent and cleaning agent additives and builders, dispersants, sequestering agents and incrustation inhibitors.

The following contains a description of a preferred method for preparing the copolymers according to the present invention.

In this preferred method, the copolymers are prepared by grafting acid-functional monomers onto polyalkylene oxide substrates by way of an aqueous polymerization process utilizing water-soluble, free-radical forming initiators and a metal salt.

Although the mechanism of the process set forth herein is not fully understood, it is believed that the metal salts used in the grafting reaction act as polymerization moderators, that is they control the molecular weight, the chain length and the degree of branching of the grafted side chain. It is further believed that the polymerization moderators lead to the formation of short, unbranched graft chains and therefore to a more biodegradable chain. This is analogous to the above-mentioned branched alkyl benzene sulfonates (ABS) that were replaced by their linear counterparts (LAS) to improve biodegradability. Even though a linear side chain is preferred for the copolymers of this invention, chains with a greater amount of branching which may not be as biodegradable, may be adequate for the uses described herein. The theory of this invention is presented here as a possible explanation of the surprising results obtained and in no way is intended to limit the scope of this invention.

The starting substrates, onto which the acid-functional monomers can be grafted, are biodegradable and include polyalkylene oxides and polyalkoxylated materials having a number average molecular weight ( $M_n$ ) of from about 100 to 100,000, and more preferably from about 200 to 10,000, and are preferably based on ethylene oxide, propylene oxide, butylene oxide, or combinations thereof. Examples of biodegradable grafting substrates include polyethylene oxides, polypropylene oxides, polybutylene oxides, polystyrene oxides, copolymers of alkylene oxides, ethers and esters of polyalkylene oxides, and polyethoxylated castor oils. The preferable substrates are polyethylene oxides, alkyl and aryl polyethoxylates, polyethoxylated castor oils and copolymers of ethylene oxide and propylene oxide. The more preferred substrate is polyethylene oxide. The weight ratio of substrate polymer to acid-functional monomer is preferably 1:20 to 5:1, more preferably 1:10 to 1:1.

Monomers useful for grafting onto the substrate, eg as side chains, can contain as polymerized units:

- (a) acid-functional ethylenically unsaturated monomers such as acrylic acid, methacrylic acid, maleic acid, itaconic acid, crotonic acid, vinyl acetic acid, acryloxypropionic acid, related monomers, or combinations thereof, and
- (b) 0 to 35%, eg 0 to 30%, based on the total weight of the substrate and depending on the limit of their solubility, other water-soluble or water-insoluble ethylenically unsaturated monomers copolymerizable with (a), for example: alkyl esters of acrylic or methacrylic acids such as methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and isobutyl methacrylate; hydroxyalkyl esters of acrylic or methacrylic acids such as hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate, and hydroxypropyl methacrylate; acrylamide; methacrylamide; N-tertiary butyl acrylamide; N-methyl acrylamide; N,N-dimethyl acrylamide; acrylonitrile; methacrylonitrile; allyl alcohol; allyl sulfonic acid; allyl phosphonic acid; vinylphosphonic acid; dimethylaminoethyl acrylate; dimethylaminoethyl methacrylate; phosphoethyl methacrylate; N-vinyl pyrrolidone; N-vinylformamide; N-vinylimidazole; ethylene glycol diacrylate; trimethylolpropane triacrylate; diallyl phthalate; vinyl acetate; styrene; vinyl sulfonic acid and its salts; 2-acrylamido-2-methyl propane sulfonic acid (AMPS) and its salts; or combinations thereof. Preferably the acid-functional monomer is acrylic acid.

Initiators useful in the production of the graft copolymers include the well known water-soluble, free-radical forming compounds. The preferred water-soluble initiators which may be used are peroxy, persulfate, perphosphate and azo initiators including hydrogen peroxide, t-butyl hydroperoxide, sodium persulfate, potassium persulfate, ammonium persulfate, sodium perphosphate, ammonium perphosphate, potassium perphosphate, 2,2-azobis (cyanovaleric acid), or combinations thereof. The more preferred initiators are hydrogen peroxide and tertiary butyl hydroperoxide. The initiator concentration is normally between 0.5% and 25%, preferably from 1 to 10%, by weight based on the total weight of the monomers.

The water-soluble metal salts, such as the salts of copper, iron, cobalt and manganese, are preferably employed at very low levels of from about 1 to 200 parts per million (ppm), more preferably from about 5 to 100 ppm, of the metal ion, based on the weight of the acid-functional polymerizing monomers. The mor

preferred metal salts are the copper salts, which include all inorganic and organic compounds that will generate copper ions in aqueous solution. Among suitable copper salts are: copper sulfate, copper nitrate and copper chloride. Suitable organic copper compounds include: copper acetate and inert, water-soluble copper complexes. The copper salts may be used as a sole source of metal or in combination with other transition metal salts. The amount of metal ion present during the reaction is important to the graft polymerization process. If the level of metal ion is too high, the percent monomer conversion decreases to an unacceptably low level, and if the level of metal ion is too low, the effect of molecular weight control as described above is diminished.

Polymerizations are preferably run with partial in-process neutralization. Typical levels of neutralizers are from 20 to 95 equivalent % of base, more preferably from 20 to 80 equivalent % of base, based on the acid functionality of the monomer. Examples of in-process neutralizers include sodium, potassium or ammonium hydroxide or amines, such as triethanolamine. When used, these neutralizers are added to the polymerization reaction as an aqueous solution.

The graft polymerization can be run using a batch process or a continuous process and is preferably run at a solids level of from 10 to 90% by wt, more preferably from 35 to 65% by wt. The polymerization reaction is preferably run at a temperature of from about 60 to 150 °C and more preferably from about 80 to 130 °C. An example of a batch process involves placing an aqueous solution of the graft substrate in a reaction vessel and adding the metal salt thereto. The solution is heated and then an aqueous solution of one or more monomers, a solution of initiator and a neutralizing solution are added to the reaction vessel over a period of several hours. An alternate variation involves combining two or more of the solutions prior to addition to the reactor, and a further alternative involves the addition of any comonomers as separate solutions. The addition rates may be from 1 to 10 hours, and preferably from 1 to 5 hours.

In the continuous process, the reactor is normally initially charged only with water or an aqueous solution of the metal salt and is heated to an increased temperature. The metal salt may optimally be simultaneously cofed into the reaction vessel or contained in the initial charge, or both. Grafting substrates, monomers, initiator and neutralizer may then be added at a substantially uniform rate, whereby a substantially uniform rate may include the simultaneous, linear addition of the cofeed solutions or the addition of the cofeed solutions at slightly different rates and times. Preferably, four solutions are cofed into the reaction vessel: (1) the monomer solution; (2) the graft substrate solution; (3) the initiator solution; and (4) the neutralizer solution. A satisfactory alternative variation involves combining two or more of the four solutions prior to addition to the reactor, and a further alternative involves the addition of any comonomers as separate solutions. The rate and time of addition of the monomers and initiator can be varied to account for the difference in reactivity of the monomers and thereby maximize the conversion of the monomers. For this continuous process, the residence time is from 0.25 to 5 hours, more preferably from 0.5 to 2 hours.

The above copolymers are useful as detergent and cleaning agent additives, as dispersants, or as water-treatment chemicals. The graft copolymers can be used as described above or, optionally, the end groups of polyalkylene oxides can be blocked, whereby the free OH groups of the polyalkylene oxides can be etherified, esterified, acetalized and/or aminated. Detergent and cleaning compositions of the present invention may be in any of the usual physical forms, such as powders, beads, flakes, bars, tablets, noodles, liquids, pastes, and the like. The detergent and cleaning compositions can be prepared and utilized in the conventional manner and are usually based on surfactants and, optionally, on either precipitant or sequestrant builders.

Suitable surfactants are, for example: anionic surfactants, such as C<sub>8</sub> to C<sub>12</sub> alkylbenzenesulfonates, C<sub>12</sub> to C<sub>16</sub> alkane sulfonates, C<sub>12</sub> to C<sub>16</sub> alkylsulfates, C<sub>12</sub> to C<sub>16</sub> alkylsulfosuccinates and C<sub>12</sub> to C<sub>16</sub> sulfated ethoxylated alkanols; and nonionic surfactants, such as C<sub>6</sub> to C<sub>12</sub> alkylphenol ethoxylates, C<sub>12</sub> to C<sub>20</sub> alkanol alkoxylates, and block copolymers of ethylene oxide and propylene oxide. Optionally, the end groups of polyalkylene oxide surfactants can be blocked, whereby the free OH groups of the polyalkylene oxides can be etherified, esterified, acetalized and/or aminated. Another modification consists of reacting the free OH groups of the polyalkylene oxides with isocyanates. Suitable nonionic surfactants also include C<sub>4</sub> to C<sub>18</sub> alkyl glucosides as well as the alkoxylated products obtainable therefrom by alkoxylation, particularly those obtainable by reaction of alkyl glucosides with ethylene oxide. The surfactants usable in detergents and cleaning agents can also have an amphoteric character and they can be soaps.

In general, the surfactants constitute from 2 to 50, preferably 5 to 45, wt %, by weight of the detergent or cleaning formulation. Liquid detergents and cleaning agents usually contain, as components, liquid or even solid surfactants which are soluble or at least dispersible in the detergent/cleaning formulation. Surfactants suitable for this purpose include the products that can also be used in powdered detergents/cleaning agents and, furthermore, liquid polyalkylene oxides or polyalkoxylated compounds.

Examples of sequestrant builders, which may be present in the detergent and cleaning agents of the

present invention, include phosphates; specifically, orthophosphates, pyrophosphates and especially sodium tripolyphosphate. Further examples are the zeolites, sodium carbonate, polycarboxylic acids, nitrilotriacetic acid, citric acid, tartaric acid, the salts of the aforesaid acids and the monomeric, oligomeric or polymeric phosphonates.

5 The amounts of the individual substances used in the preparation of detergent/cleaning formulations (ie by weight based on the total weight of the detergent/cleaning formulation) are, for example, up to 85% sodium carbonate, up to 45% phosphates, up to 40% zeolites, up to 30% nitrilotriacetic acid and phosphonates, and up to 30% polycarboxylic acids. Because of the severe environmental pollution caused by the use of phosphates, the phosphate content of detergent and cleaning agent formulations is being  
10 reduced so that detergents currently contain less than about 30% of phosphates, or preferably are phosphate-free. In certain liquid detergent markets the use of builders is usually limited to citric acid and its salts or a combination of citrate and fatty acid soap, while in other markets liquid detergent compositions incorporate an intermediate level of soap, (eg, about 15%), or tripolyphosphate, (eg, about 20%), to assist overall cleaning efficacy.

15 Other common additives to detergent and cleaning agent formulations are bleaching agents, eg, used in an amount of up to 30 wt %, corrosion inhibitors, such as silicates, eg, used in an amount of up to 25 wt %, and graying inhibitors, eg, used in an amount of up to 5 wt %. Suitable bleaching agents are for example, perborates, percarbonates or chlorine-generating substances, such as chloroisocyanurates. Suitable silicates used as corrosion inhibitors are, for example, sodium silicate, sodium disilicate and sodium metasilicate.  
20 Examples of graying inhibitors are carboxymethylcellulose, methylcellulose, hydroxypropylmethylcellulose and graft copolymers of vinyl acetate and polyalkylene oxides having a molecular weight of 1000 to 15,000. Other common detergent additives optionally used are optical brighteners, enzymes and perfumes. Powdered detergent/cleaning formulations may, for example contain up to 50 wt % of inert diluent or carrier, such as sodium sulfate, sodium chloride, or sodium borate. The powdered detergent/cleaning  
25 formulations can be anhydrous or they can contain small amounts, for example up to 10 wt %, of water. Liquid detergent/cleaning formulations usually contain up to 80 wt % water as an inert carrier or diluent.

The above-described biodegradable graft copolymers can be added to all detergent and cleaning agent formulations and may be used in amounts of from 0.5 to 50%, for example 5 to 50%, preferably between 0.5 and 30%, and more preferably between 1 and 15 wt %, based on the total weight of the formulation. In  
30 most cases, particularly when used as soil redeposition inhibitors, the amount of biodegradable copolymer actually used is preferably between 2 and 10 wt %, based on the detergent and cleaning agent mixture. Of particular importance is the use of the additives according to the invention in phosphate-free and low-phosphate detergents and cleaning agents, particularly those containing a precipitant builder such as sodium carbonate. The low-phosphate formulations contain up to a maximum of 25 wt % of sodium  
35 tripolyphosphate or pyrophosphate. In view of their biodegradability, the copolymers according to the invention are preferably used at high concentration in phosphate-free formulations and serve as builders in place of the phosphates.

If desired, the biodegradable copolymers according to the invention can be used in detergent/cleaning formulations together with non-biodegradable copolymers of acrylic acid and maleic acid or with acrylic acid  
40 homopolymers. The last-mentioned non-biodegradable polymers are currently being used as soil redeposition inhibitors in detergent/cleaning formulations. In addition to the aforementioned polymers, the copolymers of from C<sub>3</sub> to C<sub>6</sub> monocarboxylic and dicarboxylic acid or maleic anhydride and from C<sub>1</sub> to C<sub>4</sub> alkyl vinyl ethers are also suitable as soil redeposition inhibitors. The molecular weight of the homopolymers and copolymers is usually 1000 to 100,000. If desired, these soil redeposition inhibitors can be  
45 used in detergent/cleaning formulations, together with the biodegradable copolymers of the invention, in an amount of up to 20 wt % based on the total formulation. Although the known soil redeposition inhibitors based on the said polymers are not biodegradable, in water treatment plants they can be removed from waste water together with the activated sludge on which they are adsorbed. The biodegradable copolymers can be added to detergent/cleaning formulations in the free acid form or in completely or partly neutralized  
50 form.

Other applications for the graft copolymers of this invention include water treatment. Water treatment applications for these copolymers include dispersing applications, for example in aqueous systems, and anti-nucleating agents where minor amounts of the copolymers can serve as threshold inhibitors for crystal  
55 formation or scaling in cooling towers or boilers. Examples of dispersing applications of the graft copolymers include their use in aqueous clay dispersions for paper making. When used to inhibit crystal formation or scaling, the water-soluble copolymers are often combined with corrosion inhibitors such as inorganic or organic phosphates or phosphonates or metallic salts such as zinc compounds and the like. The copolymers of the present invention can be added directly to the aqueous system or they can be

added as a concentrated aqueous composition wherein the copolymer is present in the composition at a level of from 20% to 60% by weight.

The following examples are presented to illustrate embodiments of the present invention. Unless otherwise indicated, all percentages are weight percentages.

5

### Graft Copolymer Synthesis

#### 10 Example 1

To a two liter, 4 neck flask, equipped with a mechanical stirrer, reflux condenser, and inlets for the gradual addition of monomers, caustic solution and initiator solution were added 250 grams of deionized water, 16 grams of a 0.15% copper (II) sulfate pentahydrate aqueous solution and 100 grams of  
 15 polyethylene glycol (Mw = 3400). This solution was heated to reflux and then 250 grams of glacial acrylic acid, an initiator solution of 83.3 grams of 30% hydrogen peroxide and a base neutralizer solution of 208 grams of a 50% solution of sodium hydroxide (75 eq. % neutralized) were added linearly and separately over two hours. Once the additions were complete, the system was kept at reflux for an additional twenty minutes. The system was then cooled to 60° C, and 49.3 grams of a 50% sodium hydroxide solution was  
 20 added as a post neutralization.

The resultant polymer solution had a pH of 7.2 and a solids content of 48.2%. Based on gel permeation chromatography (GPC), the weight average molecular weight (Mw) was 4850 and the number average molecular weight (Mn) was 2060. The residual acrylic acid content was 0.01% by weight based on the total theoretical weight of solids.

25

#### Example 2

The procedure of Example 1 was repeated except that 100 grams of polyethylene glycol (Mw = 1000)  
 30 was initially added to the reactor, and 46.1 grams of a 50% sodium hydroxide solution was added for the post reaction neutralization.

The resultant polymer solution had a pH of 7.0 and a solids content of 46.9%. Based on GPC, Mw was 5000 and Mn was 3440. The residual acrylic acid content was 0.3% by weight based on the total theoretical weight of solids.

35

#### Example 3

The procedure of Example 1 was repeated except that 100 grams of polyethylene glycol (Mw = 8000)  
 40 was initially added to the reactor and 52.9 grams of a 50% sodium hydroxide solution was added for the post reaction neutralization.

The resultant polymer had a pH of 7.3 and a solids content of 45.2%. Based on GPC, Mw was 5690 and Mn was 3650. The residual acrylic acid content was 0.38% by weight based on the total theoretical weight of solids.

45

#### Example 4

The procedure of Example 1 was repeated except that 100 grams of polyethylene glycol (Mw = 400)  
 50 was initially added to the reactor, and 49.3 grams of a 50% sodium hydroxide solution was added for the post reaction neutralization.

The resultant polymer solution had a pH of 7.2 and a solids content of 44.3%. Based on GPC, Mw was 3430 and Mn was 2720. The residual acrylic acid content was <.01% by weight based on the total theoretical weight of solids.

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#### Example 5



The procedure of Example 1 was repeated except that 100 grams of polyethylene glycol ( $M_w = 3400$ ) was initially added to the reactor, the initiator cofeed was 166.6 grams of a 30% hydrogen peroxide solution and 37.9 grams of a 50% sodium hydroxide solution was added for the post reaction neutralization.

The resultant polymer had a pH of 7.2 and a solids content of 42.6%. Based on GPC,  $M_w$  was 940 and  $M_n$  was 537. The residual acrylic acid content was <.01% by weight based on the total theoretical weight of solids.

#### Example 6

The procedure of Example 1 was repeated except that 100 grams of polyethylene glycol ( $M_w = 3400$ ) and 32 grams of 0.15% copper sulfate pentahydrate solution was added to the reactor and 45.9 grams of a 50% sodium hydroxide solution was added for the post reaction neutralization.

The resultant polymer had a pH of 7.7 and a solids content of 47.7%. Based on GPC,  $M_w$  was 4750 and  $M_n$  was 3100. The residual acrylic acid content was 0.01% by weight based on the total theoretical weight of solids.

#### Example 7

The procedure of Example 1 was repeated except that 100 grams of polyethylene glycol ( $M_w = 1000$ ) and 32 grams of 0.15% copper sulfate pentahydrate solution was added to the reactor, and 45.9 grams of a 50% sodium hydroxide solution was added for the post reaction neutralization.

The resultant polymer had a pH of 7.7 and a solids content of 45.6%. Based on GPC,  $M_w$  was 4250 and  $M_n$  was 3000. The residual acrylic acid content was <.01% by weight based on the total theoretical weight of solids.

#### Example 8

The procedure of Example 1 was repeated except that 200 grams of polyethylene glycol ( $M_w = 1000$ ) and 400 grams of deionized water was added to the reactor and 45.9 grams of a 50% sodium hydroxide solution was added for the post reaction neutralization.

The resultant polymer had a pH of 5.7 and a solids content of 45.7%. Based on GPC,  $M_w$  was 4950 and  $M_n$  was 3480. The residual acrylic acid content was <.01% by weight based on the total theoretical weight of solids.

#### Example 9

The procedure of Example 1 was repeated except that 200 grams of polyethylene glycol ( $M_w = 3400$ ), 400 grams of deionized water and 32 grams of a 0.15% copper pentahydrate solution was added to the reactor and 45.0 grams of a 50% sodium hydroxide solution was added for the post reaction neutralization.

The resultant polymer had a pH of 7.4 and a solids content of 45.1%. Based on GPC,  $M_w$  was 3760 and  $M_n$  was 2420. The residual acrylic acid content was <.01% by weight based on the total theoretical weight of solids.

#### Example 10

To a three liter, 4 neck flask, equipped with a mechanical stirrer, reflux condenser, and inlets for the gradual addition of monomers, caustic solution and initiator solution, were added 403 grams of deionized water, 26.9 grams of a 0.15% copper (II) sulfate pentahydrate aqueous solution and 168 grams of polyethylene glycol ( $M_w = 3400$ ). This solution was heated to reflux and then 420 grams of glacial acrylic acid, an initiator solution of 140 grams of 30% hydrogen peroxide and a base neutralizer solution of 349 grams of a 50% solution of sodium hydroxide (75 eq.% neutralized) were added linearly and separately over two hours. Once the additions were complete, the system was kept at reflux for an additional 30 minutes. The system was then cooled to 60°C, and 71.2 grams of a 50% sodium hydroxide solution was

added as a post neutralization.

The resultant polymer solution had a pH of 7.3 and a solids content of 45.4%. Based on GPC, Mw was 5720 and Mn was 3510. The residual acrylic acid content was less than 0.01% by weight based on the total theoretical weight of solids.

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#### Example 11

To a two liter, 4 neck flask, equipped with a mechanical stirrer, thermometer, condenser and inlets for the gradual addition of monomers, substrate, initiator and neutralizer solutions, were added 50 grams of deionized water and 16 grams of a 0.15% copper (II) sulfate pentahydrate solution. A monomer cofeed of 250 grams of glacial acrylic acid, an initiator cofeed solution of 83.3 grams of 30% hydrogen peroxide, a cofeed solution of polyethylene glycol (Mw = 3400) in 200 grams deionized water and a neutralizer solution of 208 grams (75 equivalent % neutralized) of a 50% solution of sodium hydroxide were prepared. Initially, 10% of each of the cofeed solutions were added to the flask and then the contents of the flask was heated to reflux. The remaining amounts of cofeed solution were then added linearly and separately over two hours. At the completion of the addition of the feeds, the reaction was held for 30 minutes at reflux. The reaction was then cooled to 60 °C and 49.3 grams of 50% sodium hydroxide solution was added as a post reaction neutralization.

The resultant polymer had a pH of 6.6 and a solids content of 42.4%. Based on GPC, Mw was 8110 and Mn was 2460. The residual acrylic acid content was <.01% by weight based on the total theoretical weight of solids.

#### Example 12

The procedure of Example 11 was repeated except that 66 grams of deionized water was used in the initial charge. The polyethylene glycol cofeed solution was prepared using 16 grams of a 0.15% copper (II) sulfate pentahydrate solution, 184 grams of deionized water and 100 grams of polyethylene glycol (Mw = 8000).

The resultant polymer had a pH of 7.6 and a solids content of 45.0%. Based on GPC, Mw was 7860 and Mn was 3560. The residual acrylic acid content was <.01% by weight based on the total theoretical weight of solids.

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#### Example 13

The procedure of Example 1 was repeated except that 3.9 grams of a 1% aqueous solution of ethylenediaminetetraacetic acid iron (III) monosodium salt was added to the flask in place of the copper (II) sulfate pentahydrate solution.

The resultant polymer solution had a pH of 6.5 and a solids content of 48.5%. Based on GPC, Mw was 8400 and Mn was 2880. The residual acrylic acid content was 0.62% by weight based on the total theoretical weight of solids.

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#### Example 14

The procedure of Example 1 was repeated except that 3.9 grams of a 1% aqueous solution of ethylenediaminetetraacetic acid copper (II) disodium salt was added to the flask in place of the copper (II) sulfate pentahydrate solution.

The resultant polymer solution had a pH of 6.8 and a solids content of 46.4%. Based on GPC, Mw was 6840 and Mn was 1820. The residual acrylic acid content was <0.01% by weight based on the total theoretical weight of solids.

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#### Example 15

The procedure of Example 1 was repeated except that 100 grams of Neodol C12-C15 polyethylene

oxide was added to the flask instead of the polyethylene glycol.

The resultant polymer solution had a pH of 8.7 and a solids content of 47.5%. Based on GPC, Mw was 6190 and Mn was 4230. The residual acrylic acid content was <0.01% by weight based on the total theoretical weight of solids.

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#### Example 16

The procedure of Example 1 was repeated except that 50 grams of polyethylene glycol (Mw 3400) was added to the flask. The resultant polymer had a pH of 7.3 and a solids content of 42.1%. Based on GPC, Mw was 5080 and Mn was 3470. The residual acrylic acid content was 0.05% by weight based on the total theoretical weight of solids.

#### Example 17

The procedure of Example 1 was repeated except that 16 grams of a 0.15% iron (III) sulfate heptahydrate solution was added to the flask in place of the copper (II) sulfate pentahydrate solution.

The resultant polymer had a pH of 6.7 and a solids content of 45.9%. Based on GPC, Mw was 12600 and Mn was 2300. The residual acrylic acid content was 0.22% by weight based on the total theoretical weight of solids.

#### Example 18

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The procedure of Example 1 was repeated except that 450 grams of deionized water and 500 grams of polyethylene glycol (Mw 3400) was added to the flask.

The resultant polymer had a pH of 7.1 and a solids content of 51.9%. Based on GPC, Mw was 3720 and Mn was 1380. The residual acrylic acid content was 0.06% by weight based on the total theoretical weight of solids.

#### Example 19

The procedure of Example 1 was repeated except that 250 grams of polyethylene glycol (Mw = 3400) was added to the flask.

The resultant polymer had a pH of 6.7 and a solids content of 53.1%. Based on GPC, Mw was 4480 and Mn was 2110. The residual acrylic acid content was <0.01% by weight based on the total theoretical weight of solids.

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#### Example 20

The procedure of Example 1 was repeated except that the monomer cofeed consisted of 200 grams of glacial acrylic acid and 42.4 grams of maleic anhydride. The base neutralizer solution was 218 grams of a 50% NaOH solution and the post reaction neutralization solution was 39 grams of a 50% NaOH solution.

The resultant polymer had a pH of 7.9 and a solids content of 46.5%. Based on GPC, Mw was 4880 and Mn was 1830. The residual acrylic acid content was 0.06% and the residual maleic acid content was 0.33%, both percentages being by weight based on the total theoretical weight of solids.

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#### Example 21

To a two liter, 4 neck flask, equipped with a mechanical stirrer, a reflux condenser, and inlets for the gradual additions of monomer, neutralizer and initiator solutions, were added 100 grams of deionized water, 16 grams of a 0.15% copper (II) sulfate pentahydrate aqueous solution and 100 grams of polyethylene glycol (Mw 1000). The solution was heated to reflux and then a monomer solution of 200 grams of glacial acrylic acid, 50 grams of itaconic acid and 200 grams of deionized water; a neutralizer solution of 228.3

grams of a 50% solution of sodium hydroxide in deionized water; and an initiator solution of 83.3 grams of a 30% hydrogen peroxide solution was added linearly and separately over two hours. When the feeds were complete, reflux continued for twenty minutes and then the reaction was cooled to room temperature.

The resultant polymer had a pH of 6.1 and a solids content of 45.6%. Based on GPC, Mw was 2850 and Mn was 2110. The residual acrylic acid content was 0.03% and residual itaconic acid content was 0.27%, both percentages being by weight based on the total theoretical weight of solids.

#### Example 22

The procedure of Example 1 was repeated except that 100 grams of Emulphor EL-620 ethoxylated castor oil was added to the flask instead of the polyethylene glycol. The post reaction neutralizer was 48.1 grams of a 50% solution of sodium hydroxide.

The resultant polymer had a pH of 7.0 and a solids content of 46.5%. Based on GPC, Mw was 4950 and Mn was 2940. The residual acrylic acid content was <0.01% by weight based on the total theoretical weight of solids.

#### Example 23

The procedure of Example 1 was repeated except that the monomer cofeed solution contained 125 grams of glacial acrylic acid and 125 grams of glacial methacrylic acid. The base neutralizer cofeed contained 191 grams of a 50% solution of sodium hydroxide. The post reaction neutralization solution was 38.8 grams of 50% solution of NaOH.

The resultant polymer had a pH of 7.2 and a solids content of 46.7%. Based on GPC, Mw was 6200 and Mn was 2030. The residual acrylic acid content was 0.56% and residual methacrylic acid content was 0.16%, both percentages being by weight based on the total theoretical weight of solids.

#### 30 Biodegradation Testing

The biodegradabilities of some of the above-described graft copolymers are listed in the Tables below. Polymer biodegradabilities were measured on a scale of 0 to 100% based on BOD (biological oxygen demand) testing, the CO<sub>2</sub> produced and the dissolved organic content (SCAS). The results are in Tables II and III. The BOD procedure is the method in Standard Methods for Examination of Water & Wastewater page 525, 16th edition (1985) and the SCAS and CO<sub>2</sub> tests were done according to the procedures in, OECD Guidelines for Testing of Chemicals, (modified Strum method, CO<sub>2</sub> test No. 301B, SCAS test No. 302A).

The BOD test used was a closed bottle test whereby a solution of the candidate polymers and mineral salts is inoculated with municipal sewage bacteria. Biodegradation was indicated by oxygen uptake, which was determined by measuring the dissolved oxygen content of the solution. BOD test results provided are for 5 mg/300 ml concentrations and are for the durations listed. The CO<sub>2</sub> test results are for 10 mg/300 ml and the SCAS test results are for 20 mg/300 ml.

#### 45 Powdered Detergent Formulation and Performance Evaluation

A 10.16cm x 10.16cm (4" x 4") white cotton swatch was soiled with approximately 1 gram of a 50% slurry (in water) of Skippack clay. The soil, covering a 5.08cm (2") diameter circle centered on the swatch, is allowed to air dry overnight. Clean fabric (for redeposition test) was a 10.16cm x 10.16cm (4" x 4") white cotton swatch which was unsoiled.

The detergent compositions were tested in a Terg-o-Tometer at the following conditions; 40 °C, 100 rpm, 100 ppm hardness (50% city tap water/50% de-ionized water), 12 minute wash with one 3 minute rinse, 1300 ppm detergent and 5 cloths per pot (3 of them soiled). The wash water was pre-heated, the fabric swatches were added and then dissolved detergent (2.6 grams of a 50% slurry in 100 mls water) was added. Following the wash period the swatches were wrung, and following the rinse cycle the swatches were wrung again and then air dried. Swatches washed in a detergent containing polyacrylic acid homopolymer were always run as a control.

Reflectance was measured using a Pacific Scientific Colorimeter (Colorgard System 1000) and the data recorded using the L,a,b color scale. Detergency values (E) and whiteness index (W.I.) are calculated as:

$$E = V(L_s - L)^2 + (a_s - a)^2 + (b_s - b)^2$$

$$W.I. = L/100(L - (5.715 \times b))$$

where  $L_s$ ,  $a_s$ , and  $b_s$  are the reflectivity reading for the soiled swatches and  $L$ ,  $a$ ,  $b$  are the reflectivity readings for the washed swatches.

Each polymer was evaluated in three separate washing experiments. The detergent composition shown in Table I was used for the above-described performance evaluation and the results of the detergent performance evaluation are listed in Tables II and III along with the BOD biodegradation data. Additional possible powdered detergent formulations, which may contain the polymers of this invention, are presented, but not limited to, the formulations as shown in Table IV.

Table I  
Powdered Detergent Composition Used to Evaluate  
the Polymers of this Invention

<u>Detergent Component</u>	<u>Amount, %</u>
sodium carbonate	22.0
zeolite A	16.0
sodium silicate	2.7
LAS	8.3
lauryl sulfate	8.3
sodium sulfate	34.0
polymer	1.7
water	7.0

Table II

## Biodegradation, Clay Soil Removal and Redeposition Test Data

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<u>EXAMPLE</u>	<u>BIODEGRADATION</u>		<u>DETERGENCY, E</u>	<u>REDEPOSITION, W.I.</u>
	<u>BOD, %</u>	<u>Days, No.</u>		
1	37.4	37	39.9	78.3
2	70.6	47	40.3	69.8
3	73.0	47	40.2	70.0
4	13.7	14	40.2	69.6
5	29.5	47	40.0	71.1
6	49.1	52	39.5	70.8
8	63.5	52	37.3	68.2
9	100.4	52	40.0	70.7
11	52.0	54	40.5	71.0
12	44.5	54	40.0	70.7

20

25

Table III

<u>Example</u>	<u>Biodegradation, %</u>	
	<u>CO<sub>2</sub></u>	<u>SCAS</u>
1	19.4	44.6
6	41.0	31.2

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TABLE IV  
POWDER COMPOSITIONS

	<u>TPP<sup>1</sup></u>	<u>PYRO<sup>2</sup></u>	<u>Phos- phate</u>	<u>NON- Phos- phate</u>
5				
10				
Anionic				
LAS <sup>3</sup>	5	5	6	7.5
Lauryl Sulfate	8	13	—	—
Alcohol Ether Sulfate	3	—	—	—
15				
PEO <sup>4</sup> Alcohol	1.5	2	—	—
TPP	38	30	30	—
Pyro	—	13	—	—
20				
Sodium Carbonate	10	24	7	7.5
Sodium Sulfate	15	5	15	20
Sodium Silicate	6	—	5	1.5
Zeolite A	—	0.2	—	25
25				
Opt. Brightener	0.2	0.5	0.2	0.2
Enzyme	0.5	0.7	0.3	0.3
NaPAA <sup>5</sup>	—	—	—	—
Soap	—	—	1	—
Nonionic (EO/PO <sup>6</sup> )	—	—	5	5
30				
Perborate	—	—	20	22.5
TAED <sup>7</sup>	—	—	4	—
Anti-Redep. Agents	—	—	0.2	0.2
Sulfate	—	—	0.5	0.3
35				
Water				
40				
1 Sodium Tripolyphosphate				
2 Sodium Pyrophosphate				
3 Linear Alkyl Sulfonates				
4 Polyethoxylate				
5 Sodium salt of polyacrylic acid				
6 Ethylene Oxide/Propylene Oxide				
45				
7 Tetraacetyl Ethylene Diamine				

Liquid Detergent Formulation and Performance Evaluation

50 The efficacy of the polymers of this invention in a liquid detergent formulation was evaluated by washing cotton, polyester/cotton blend (65/35) and polyester soiled fabrics in a commercially available, heavy duty liquid composition utilizing Sears Kenmore Ultra Fabric Care brand washing machines (model Heavy Duty 80 Series) set to typical U.S. laundering parameters. Washing conditions, soil/fabric combina-  
55 tions and polymer concentration are detailed in Tables V and VI, and the liquid detergent formulation base used for evaluating the copolymers of the invention is, for example, that shown in EP-A-0 348 183 and depicted in Table VII. Table VIII shows other suitable formulations for liquid detergents which are possible, but not limiting, for use with the copolymers of the invention.

Soiled cloths were prepared (except where noted) by Scientific Services (Oakland, NJ) and cut to a specified size [8.89cm x 11.43cm (3 1/2" x 4 1/2")]. Reflectance was measured using a Pacific Scientific Colorimeter (Colorgard System 1000) and the data recorded using the L,a,b color scale. The reflectance (L) of the soiled cloths was measured before laundering so that only cloths of the same reflectance were used in a test. Reflectance was then measured after laundering to evaluate the efficacy of the detergent and are reported as the average value. In an effort to create realistic soil/fabric combinations encountered in a consumer's wash load, soils were selected from four classes;

- Particulates (clays)
- Oily/Particulates (collar soils)
- Oxidizables (stains)
- Enzyme Sensitive (proteinaceous).

Unsoiled cotton swatches and unsoiled polyester swatches were included in the tests to assess the antiredeposition characteristics of the individual polymers. Each soil/fabric combination was evaluated with four replicates. The data were derived by averaging the reflectance values from all of the swatches stained with a given soil and appear in Table IX.

TABLE V

## WASH CONDITIONS:

APPARATUS - SEARS KENMORE BRAND WASHING MACHINE

TEMPERATURE - WARM (95°F)

HARDNESS - CONVENTIONAL (120 PPM)

AGITATION - HIGH

WASH CYCLE - MEDIUM (10 MIN.), 63.21 LITRES/LOAD (16.7

GALLONS/LOAD)

DETERGENT DOSAGE - RECOMMENDED LEVEL - 1/2 CUP (130 GRAMS)

POLYMER CONCENTRATION - 5% SOLIDS (NEUTRALIZED, pH 7)



Table VI

5	<u>SOIL CLASS</u>	<u>SOIL IDENTITY (SWATCH FABRIC)</u>
10	PARTICULATES	*BIG OAK CLAY (COTTON) *SKIPPACK CLAY (COTTON) SCIENTIFIC SERVICES CLAY (COTTON)
15	OILY/PART.	COSMETIC MAKEUP (COTTON) DUST/SEBUM (COTTON, PE/COTTON, PE)
20	OXIDIZABLE	GRAPE JUICE (PE/COTTON) BREWED TEA (PE/COTTON) GRASS (COTTON)
25	ENZYME	CHOC. FUDGE PUDDING (PE/COTTON)
30	REDEPOSITION	COTTON POLYESTER
35	* Prepared by applying 0.7 - 0.8 grams of a 25% clay slurry (in water) of Skippack or Big Oak Clay to a 8.89cm x 11.43cm (3 1/2" X 4 1/2") white cotton swatch (Cotton #405 - Test Fabrics) using a China bristle brush (#10). The soil was "painted" onto the cloth inside a 5.08cm (2") diameter circle and allowed to air dry overnight prior to laundering.	
40		
45		
50		
55		

Table VII  
BASE LIQUID DETERGENT FORMULATION

<u>Component</u>	<u>% by weight</u>
Surfactants	
Linear Dodecylbenzene Sulfonate	17.00
Alcohol Ethoxylate (Nonionic)	7.00
Builder	
Sodium Citrate	10.00
Hydrotrope/Solubilizing Agent	
Monoethanolamine	2.00
Miscellaneous*/Water	Composition made up to 100%

\*Includes perfumes, colourants, fatty acids, whiteness and opacifiers.

Table VIII  
LIQUID COMPOSITIONS

	Unbuilt	Citrate	Citrate/Fatty Acid Soap	Phos- phate	Non- Phos- phate
LAS	3.5	15	8	7	19
Alc. Ether Sulfate	---	---	16	---	---
Citrate	---	10	6	---	---
Fatty Acid Soap	---	---	10	---	---
Nonionic Surfactant	16	7.5	6	3	15
Propylene Glycol	---	---	8	---	4
Ethanol	5	---	4	---	8.5
Na Xylene Sulfonate	---	5.5	---	---	---
Opt. Brightener	0.2	0.2	0.15	0.1	0.25
Enzyme	0.7	---	0.5	0.5	0.75
Water	Q.S.*	Q.S.*	Q.S.*	Q.S.*	Q.S.*
Borax	---	---	---	3	---
Tripolyphosphate	---	---	---	23	---
Glycerin	---	---	---	6	---

\*Q.S. = composition made  
up to 100% with  
water

TABLE IX

Reflectance (L) Values with 5% Polymer

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<u>Polymer</u>	<u>STAIN</u>				<u>REDEPOSITION</u>	
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>
None	80.7	81.9	79.4	90.0	99.2	74.4
Example 1	80.9	82.3	78.4	90.2	92.2	n/a
Example 4	81.9	83.0	80.0	90.7	93.0	74.1
Example 9	81.4	82.7	79.2	90.0	96.4	73.8
Example 11	81.2	82.9	78.6	90.3	97.9	73.4

A) Oily Particulate Stain

B) Oxidizable Stain

C) Particulate Soil

D) Enzymes

E) Redeposition on Cotton (Whiteness Index)

F) Redeposition on Polyester (Whiteness Index)

Scale Inhibition

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The efficacy of the polymers of the invention as a calcium carbonate ( $\text{CaCO}_3$ ) anti-precipitant was evaluated as follows:

1. To a 113.4g (four ounce) jar was added

a) 50 ml of a solution of

600 mg/l  $\text{Na}_2\text{CO}_3$  as  $\text{CaCO}_3$

600mg/l  $\text{NaHCO}_3$  as  $\text{CaCO}_3$

b) 0.7 ml of 0.1% by weight polymer solids (at pH 8.0)

c) 50 ml of a solution of

1200 mg/l  $\text{CaCl}_2$  as  $\text{CaCO}_3$

600 mg/l  $\text{MgSO}_4$  as  $\text{CaCO}_3$

2. The jar was capped and placed in a 54° C water bath for twenty hours.

3. The hot samples were filtered through a 0.45 micrometer filter.

4. The filtrate was titrated with ethylenediaminetetraacetic acid (EDTA).

55

$$\% \text{ CaCO}_3 \text{ INHIBITION} = \frac{A - C}{B - C} \times 100$$

where A is the level in mg/l of  $\text{Ca}^{2+}$  in the filtrate after precipitation, B is the level in mg/l of  $\text{Ca}^{2+}$  in the sample before precipitation, and C is the level in mg/l of  $\text{Ca}^{2+}$  in the sample with no polymer after precipitation. The data appear in Table X.

The efficacy of the polymers of this invention as a phosphate anti-precipitant was evaluated as follows:

1. To a 113.4g (four ounce) jar was added
  - a) 40 ml of a solution of 500 mg/l  $\text{NaHCO}_3$  as  $\text{CaCO}_3$
  - b) 20 ml of a solution of 25 mg/l  $\text{Na}_2\text{HPO}_4$  as  $\text{PO}_4^{3-}$
  - c) 1.0 or 1.5 ml of 0.1% by weight polymer solids (at pH 8.0)
  - d) 40 ml of a solution of
    - 1000 mg/l  $\text{CaCl}_2$  as  $\text{CaCO}_3$
    - 500 mg/l  $\text{MgCl}_2$  as  $\text{CaCO}_3$
    - e) 0.2 ml of a solution of 250 mg/l  $\text{FeCl}_3$  as  $\text{Fe}^{3+}$
2. The pH was adjusted to 8.5 with dilute NaOH
3. The jar was capped and placed in a 49 ° C water bath for twenty hours.
4. Hot samples were filtered through a 0.45 micrometer filter.
5. The filtrate was analyzed for phosphate using the ascorbic acid method (APHA standard 13th edition p. 532, 1971).

$$\% \text{ PO}_4^{3-} \text{ INHIBITION} = \frac{A - C}{B - C} \times 100$$

where A is the level in mg/l of  $\text{PO}_4^{3-}$  in the filtrate after precipitation, B is the level in mg/l of  $\text{PO}_4^{3-}$  in the sample before precipitation, and C is the level in mg/l of  $\text{PO}_4^{3-}$  in the sample with no polymer after precipitation. The data appear in Table X.

The efficacy of the polymers of the invention as a dispersant was evaluated as follows:

1. To a Cowles mixing cup were added:
  - 320 ml of 200 mg/l of 200 mg/l  $\text{CaCl}_2$  as  $\text{CaCO}_3$
  - 0.32 g of Hydrite UF Kaolin Clay (1000 mg/l Kaolin)
2. The mixture was stirred at high speed for ten minutes.
3. The pH was adjusted to 7.5 with dilute NaOH.
4. 100 ml aliquots were placed in 113.4g (four ounce) jars
5. 1 ml of a 0.1% polymer solution (adjusted to pH 8) was added to each aliquot.
6. The jars were capped and placed on a shaker at low speed for 10 minutes.
7. The samples were transferred to graduated cylinders and stood undisturbed for three hours.
8. The top 25 ml of each sample were transferred to a 28.35g (one ounce) vial.
9. The turbidity of each sample was measured in Nephelometric Turbidity Units (NTU's)

$$\% \text{ KAOLIN DISPERSANCY} = \frac{A - C}{B - C} \times 100$$

where A is the turbidity in NTU's of the sample after three hours, B is the turbidity in NTU's of the sample immediately after agitation, and C is the turbidity in NTU's of a control sample containing no polymer after three hours. The data appear in Table X.

TABLE X

Polymer Dosage	% CaCO <sub>3</sub> Inhibition		% PO <sub>4</sub> <sup>3-</sup> Inhibition	% Kaolin Dispersancy	
	5mg/l	10mg/l	10mg/l	15mg/l	10mg/l
none	0	0	0	0	0
Example 1	39	34	0	3	30
Example 9	34	37	8	73	75
Example 4	36	40	38	40	59

#### Hard Surface Cleaner: Formulation and Performance Evaluation

Dishwashing tests were performed using a modified version of A.S.T.M. method D 3556-85, Standard Test Method for Deposition on Glassware During Mechanical Dishwashing. This test method covers a procedure for measuring performance of household automatic dishwashing detergents in terms of the build-up of spots and film on glassware. Glass tumblers were given multiple cycles in a dishwasher, in the presence of food soils, and the levels of spotting and filming allowed by the detergents under test were compared visually.

A Kenmore brand dishwashing machine was used to perform the washing tests. The bottom rack of the dishwasher was randomly loaded with 10-12 dinner plates and the top rack was randomly loaded with several beakers and cups. Four new 283.5g (10 ounce) tumblers were placed randomly on the top racks as the test glasses. Soil used in the test was a mixture of 80% margarine and 20% non-fat dry milk. The amount of soil used for each test was 40 grams for the first wash of each complete cycle.

When a test was ready to be started, the soil was smeared across the four plates on the bottom rack, the detergent for the first cycle was placed in the detergent dispenser cup, and the machine was started. The dishwashing machines had a short and a long cycle. The experiments were conducted using three consecutive long cycles, i.e. normal washes, each of which consisted of a wash, a rinse, a second wash, two more rinses, and then a drying cycle. During the normal wash, at the start of the second wash (about twelve minutes into a normal cycle), the machine was opened and a second detergent aliquot added. Additional soil was not added at the time when a second detergent dose was added. The machine was then allowed to run the full cycle including the drying time.

When the drying cycle was completed, the door was opened and the four glasses were removed and evaluated for filming and spotting. The test glasses were evaluated by placing them in light box equipped with a fluorescence light. The glasses were ranked according to the following scale:

<u>Filming</u>		<u>Spotting</u>	
0	No film	0	No spots
1	Barley perceptible	1	Random
2	Slight	2	1/4 of glass
3	Moderate	3	1/2 of glass
4	Heavy	4	Complete spotting

An average filming and spotting rating was derived from the individual ratings by adding all the ratings for each glass per cycle, dividing by the number of glasses, then multiplying times the number of cycles. This numerical rating gave a good indication of the overall performance for each detergent tested. It was also noted if streaking existed or calcium deposits were present.

The water hardness conditions for the supply water to the dishwasher was 200 ppm. The temperature of the supply water was maintained at 48.9°C (120°F).

The detergents tested were based on Vert (Consumer product from Canada-Loblaws) which is a phosphate-free, chlorine-free formulation comprising about 12% Na<sub>2</sub>SO<sub>4</sub>, 16% H<sub>2</sub>O, less than about 40%

Na<sub>2</sub>CO<sub>3</sub>, silicate, citrate. When evaluations with chlorine were done, 1% by weight of the formulation of NaOCl was added. The results appear in Table XI.

Table XI

	% Chlorine Available	% Polymer	Third Cycle		Average	
			Film	Spot	Film	Spot
5	0	0				
10	1	0	4.0	4.0	2.2	3.2
	1	2% polyacrylic acid*	2.5	0.5	1.6	0.5
15	1	2% Example 10	0.2	0.0	0.2	0.4
	1		0.5	0.7	0.3	0.4

\*Neutralized, spray-dried homopolymer of acrylic acid with average molecular weight of 4,500. weight

The following are trademarks:

Neodol  
Emulphor  
25 Kenmore

#### Claims

- 30 1. A biodegradable water-soluble graft copolymer having building, dispersing and threshold inhibiting properties, which comprises (a) one or more acid-functional monomer, and, optionally, (b) one or more other ethylenically unsaturated monomer copolymerizable with (a), said monomer or monomers being grafted to a biodegradable substrate, said substrate being selected from polyalkylene oxides, polyalkoxylated materials and mixtures thereof, and said copolymer being at least 25 percent biodegradable.
- 35 2. A copolymer as claimed in claim 1 wherein:
  - i) the weight ratio of the biodegradable substrate to acid-functional monomer(s) (a) is from about 1:20 to 5:1,
  - ii) the weight of monomer(s) (b) is from 0 to 35 percent, based on the total weight of said substrate,
  - 40 and
  - iii) monomer(s) (a) and, if present, monomer(s) (b) form a side chain on said substrate.
- 45 3. A graft copolymer as claimed in claim 1 or claim 2, wherein said acid-functional monomer(s) (a) is selected from acrylic acid, methacrylic acid, maleic acid, itaconic acid, crotonic acid, vinyl acetic acid, acryloxy propionic acid, and combinations thereof.
- 50 4. A graft copolymer as claimed in any preceding claim, wherein said ethylenically unsaturated monomer(s) (b) copolymerizable with (a), is selected from alkyl acrylates and methacrylates, hydroxyalkyl acrylates and methacrylates, acrylamide, methacrylamide, N substituted amides, styrene, vinyl acetate, vinyl ethers, acrylonitrile, and combinations thereof.
5. A graft copolymer as claimed in any preceding claim, wherein said substrate is selected from polymers based on ethylene oxide, propylene oxide, butylene oxide, or combinations thereof.
- 55 6. A composition, which comprises:
  - i) a graft copolymer as claimed in any of claims 1 to 5; and
  - ii) an inert carrier or diluent, eg water.

7. A composition as claimed in claim 6, which is in the form of a detergent or cleaning composition and wherein:
  - a) said composition is a liquid and said inert carrier or diluent is water; or
  - b) said composition is a powder and said inert carrier or diluent is selected from sodium sulfate, sodium chloride, and sodium borate.
8. A composition as claimed in claim 6 or claim 7, which is in the form of a detergent or cleaning composition and in which the graft copolymer (i) is present in an effective amount to serve as a detergent builder or anti-incrustation agent.
9. A composition as claimed in claim 8, wherein
  - I) the graft copolymer (i) is present as a detergent builder and is present in an amount of from 5 percent to 50 percent by weight of the composition; or
  - II) the graft copolymer (i) is present as an anti-incrustation agent and is present in an amount of between 1 percent and 10 percent by weight of the composition.
10. The use of a detergent or cleaning composition as claimed in any of claims 7 to 9 as a laundry detergent or as a hard surface cleaner.
11. A composition as claimed in claim 6 which is in the form of a water treatment composition, and wherein the inert carrier or diluent is water.
12. A composition as claimed in claim 6 or claim 11 which is in the form of a water treatment composition and in which the graft copolymer (i) is present at a concentration of from 20 percent to 60 percent, based on the total weight of said composition.
13. The use of a composition as claimed in claim 11 or claim 12 as an incrustation inhibitor, or in aqueous systems as a dispersant.
14. The use of a copolymer as claimed in any of claims 1 to 5 as an incrustation inhibitor, or in aqueous systems as a dispersant.
15. A process for making a biodegradable water-soluble graft copolymer as claimed in any of claims 1 to 5, which comprises; grafting, to a biodegradable substrate, (a) one or more acid-functional monomer, and, optionally, (b) one or more other ethylenically unsaturated monomer copolymerizable with said acid-functional monomer(s), wherein said substrate is selected from polyalkylene oxides, polyalkoxylated materials and mixtures thereof; and wherein said copolymer is at least 25 percent biodegradable.





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⑪ Publication number: **0 429 307 A3**

⑫

## EUROPEAN PATENT APPLICATION

⑪ Application number: 90312699.3

⑤ Int. Cl.<sup>5</sup>: **C08F 283/06, C08L 51/08,  
C11D 3/37, C02F 1/56**

⑫ Date of filing: 21.11.90

③ Priority: 22.11.89 US 441122

④ Date of publication of application:  
29.05.91 Bulletin 91/22

⑥ Designated Contracting States:  
**AT BE CH DE DK ES FR GB GR IT LI LU NL SE**

⑧ Date of deferred publication of the search report:  
25.03.92 Bulletin 92/13

⑦ Applicant: **ROHM AND HAAS COMPANY**  
Independence Mall West  
Philadelphia Pennsylvania 19105(US)

⑦ Inventor: **Hughes, Kathleen Anne**  
835 Cathcart Road  
Blue Bell, Pennsylvania 19422(US)  
Inventor: **Swift, Graham**  
901 Cross Lane  
Blue Bell, Pennsylvania 19422(US)

⑦ Representative: **Tanner, James Percival et al**  
**ROHM AND HAAS (UK) LTD.** European  
Operations Patent Department Lennig House  
2 Mason's Avenue  
Croydon CR9 3NB(GB)

⑤ Biodegradable, water-soluble graft copolymers, compositions containing such copolymers, and methods of use of such copolymers.

⑤ This invention is concerned with biodegradable water-soluble graft copolymers having building, anti-filming, dispersing and threshold crystal inhibiting properties, the copolymers comprising, grafted to a biodegradable substrate comprising polyalkylene oxide and/or polyalkoxylated materials, (a) acid-functional monomer(s), and, optionally, (b) other ethylenically unsaturated monomer(s) copolymerizable with (a).

The invention is also concerned with a process for preparing the graft copolymers, compositions comprising the graft copolymers, and with the use of such copolymers/compositions.

EP 0 429 307 A3



European  
Patent Office

## EUROPEAN SEARCH REPORT

Application Number

EP 90 31 2699

### DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 285 037 (BASF) * claims 1-4 ** - - - -	1-15	C 08 F 283/06 C 08 L 51/08 C 11 D 3/37 C 02 F 1/56
X	EP-A-0 098 803 (CIBA) * claims 1-3 ** - - - -	1-15	
X	EP-A-0 299 691 (DIVERSEY CORPORATION) * page 5, line 7; claim 1 ** - - - -	1-15	
X	EP-A-0 011 833 (UNION CARBIDE) * claims 1-6 ** - - - -	1-7	
X	FR-A-1 562 105 (HERCULES)the whole document - - - - -	1-7	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5)  C 08 F C 11 D
Place of search  The Hague		Date of completion of search  23 January 92	Examiner  MEULEMANS R.A.M.G.G.
<div><div><b>CATEG RY OF CITED DOCUMENTS</b> X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention</div><div>E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ----- &amp;: member of the same patent family, corresponding document</div></div>			